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CANADIAN PATENT

PROCESS FOR ~~TREATING PAPER PULP~~

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No. OF CLAIMS 9

This invention relates generally to the treatment of paper pulp and, more particularly, to a process for treating paper pulp to improve the quality of the paper produced therefrom, and especially to decrease the porosity of the paper.

Heretofore, a number of different processes have been proposed for treating paper pulp in order to improve various properties of the paper produced therefrom. Of course, the conventional treatment is simple mechanical beating or refining of the pulp to effect fibrillation or hydration thereof. However, this treatment is extremely time-consuming and costly because of the relatively high power consumption of the conventional refiners and beaters. Also, this simple mechanical treatment is incapable of improving some properties of the pulp to the extent desired for certain types of paper.

It has also been proposed to treat pulp by mixing it with an enzyme, allowing the mixture to stand for several hours, washing the enzyme out of the pulp, and then mechanically beating or refining the pulp, as described in United States Patent 2,280,307 to Diehm. However, this process is not only time-consuming, but has actually been found to degrade certain properties of the pulp, as described in more detail hereinafter. Another process proposed in the prior art is mild agitation of the pulp in an enzyme-containing bath, as described in United States Patent 3,041,246 to Bolaski et al. Although this process improves certain properties of the pulp, the rate of improvement is relatively slow, and it has practically no effect on the porosity and other properties of the resultant paper.

Rohm & Haas

It is, therefore, the main object of this invention to provide an improved process for treating paper pulp to improve the physical properties of the paper produced therefrom.

It is another object to provide such a process which increases the density and decreases the porosity of the paper for any given period of beating or refining.

It is a further object to provide such a process which increases the rate of increase of the burst factor and breaking length of the pulp during the beating and refining process.

Other aims and advantages of the invention will be apparent from the following description and appended claims.

In the drawings:

Figs. 1, 2, and 3 are graphic illustrations of the improved results obtained in one example of the process;

Figs. 4, 5, and 6 are graphic illustrations of the improved results obtained in another example of the process; and

Fig. 7 is a graph showing the decreased porosities produced by the process of the invention at various power input rates and various levels of accumulated power input.

As used herein, the following terms have the following meanings:

The term "enzyme" refers to both pure enzymes and enzyme systems.

The term "refining" refers to the mechanical working of a water-pulp suspension to effect fibrillation and hydration of the pulp, including the treatment commonly referred to as "beating". The refining action may be achieved in a wide variety of different equipment, the most common being jordans, beaters, and disc mills.

In accordance with the present invention, there is provided a process for treating paper pulp, which process comprises mixing the pulp with water and an enzyme, and then immediately refining the resulting mixture so as to subject the pulp to simultaneous refining and enzymatic action, whereby to improve the characteristics of paper produced from said pulp.

The present invention stems from the unexpected discovery that subjecting the paper pulp to simultaneous refining and enzymatic action produces a synergistic effect, i.e., the simultaneous action improves the porosity, density, burst factor, breaking length, and other properties at a rate

substantially greater than the additive rates achieved by the refining action and enzymatic action alone. Moreover, the inventive process makes possible the attainment of considerably lower porosities than heretofore obtainable within a reasonable length of time or without the use of permanent additives.

The enzymatic action in the inventive process may be effected by any enzyme which, when present during the refining of the pulp, improves the physical properties of the pulp to a greater extent and/or in a shorter period of time than does the refining action alone. Preferred enzymes are those classed as cellulase, pectinol, lipase, pectinase, lysozyme, amylase, pectase, and hemi-cellulase, either singly or in combination with each other. However, any other enzyme which improves the pulp properties may be used.

The paper pulp treated by this process may be any cellulosic paper-making pulp, such as sulfite wood pulp, kraft or sulfate wood pulp, straw pulp, and other chemical and semi-chemical paper pulps. The pulp is suspended in water prior to being fed into the refiner or beater, in accordance with conventional paper-making procedures. The enzyme may be added to the pulp before or after the pulp is mixed with the water, or even after the pulp slurry is fed into the beater. In most cases, it is preferred to add the enzyme in increments throughout the refining process. It is important that the enzyme and pulp be uniformly mixed, especially in the case of relatively large quantities of pulp. Most of the enzyme is removed from the pulp along with the water that is removed therefrom, and the removed enzyme may be recovered and reused. Any enzyme remaining in the pulp is killed by the heat from the rolls in the subsequent rolling operations.

Interdependent factors which determine the degree of improvement achieved by the simultaneous refining and enzymatic action of the inventive process are the enzyme concentration in the pulp being treated, the contact time between the enzyme and the pulp, and the refining rate or energy input to the pulp. The enzyme concentration in the pulp is preferably at least about ten

parts per million by weight, based on the weight of dry pulp. In general, the rate of improvement of the pulp properties increases with increasing enzyme concentrations. However, there is usually an upper limit for the enzyme concentration, beyond which the en zyme may actually have a deleterious effect on the pulp properties. This upper limit varies somewhat with the type and purity of the enzyme employed. For example, experience has shown that with an enzyme of high purity (such as "Cellase 1000"), a concentration of over 2000 parts per million by weight, based on the weight of dry pulp, has a slight deleterious effect on the pulp. As a practical matter, however, it is generally desirable for economic reasons to use the lowest possible enzyme concentration.

The contact time between the enzyme and the pulp during the simultaneous refining and enzymatic action also affects the degree of improvement achieved in the pulp properties. For example, the burst factor and breaking length generally increase with increasing contact time for a certain period, and then decrease if the simultaneous action is continued for longer periods. Porosity decreases with increasing contact time, apparently with no upper limit. The preferred contact time in any specific application depends on the other process variables, such as the type and concentration of enzyme employed, the refining rate, and the type of pulp being treated. As will be seen from the specific examples described below, the preferred contact time for any particular application can be readily determined by simple empirical tests.

The refining of the mixture of pulp, water, and enzyme is carried out in any conventional pulp beater or refining equipment. However, it is critical in the inventive process that the refining rate be carried out above a certain minimum rate. This minimum rate varies somewhat with the other process variables, such as the type of pulp, type of enzyme, and enzyme concentration, but it is necessary to refine at a minimum energy input rate sufficient to disrupt or displace the fiber structure of the pulp to enhance

intimacy of contact of the enzyme with the constituents of the fibers. Under the conditions and with the equipment described below, a minimum energy input to the pulp of about 45,000 watts per hour is required for each ton of dry pulp. Below this minimum rate, the simultaneous refining and enzymatic action has little or no effect on the rate of improvement of the pulp properties, as will be seen from the specific examples described below. Above the minimum rate, the rate of improvement of the pulp properties generally increases with increasing energy input. As is well known, the rate of energy input to the pulp depends mainly on the speed of the refining members, the pressure between the refining members, and the number of passes of the pulp through the beater.

It is important that the temperature and pH of the pulp mixture be sufficient to maintain the activity of the enzyme during the refining treatment. As is well known, there is an optimum activation range of both temperature and pH for every enzyme. Beyond the limits of these ranges, the enzyme becomes inactive, and beyond the upper limit of the temperature range, the enzyme is actually killed and cannot be revived. Of course, the activation ranges of both temperature and pH vary for different enzymes, but the temperature range is generally about 20°C to 55°C, preferably 35°C to 50°C, and the pH range is generally about 3.5 to 5.5. It is also important to avoid poisoning of the enzyme, such as by avoiding contact of the enzyme with lead or other heavy metals in the process equipment.

It has been found that if the pulp is allowed to stand after the enzyme has been added, the enzyme may have a deleterious effect on the pulp. Accordingly, it is essential that the pulp be subjected to refining action immediately after the enzyme has been added. For example, when a sulfite pulp containing about 0.5 weight per cent cellzyme (5000 ppm, based on dry weight of pulp) was allowed to stand for 6 hours and then washed clean of enzyme and refined for 40 minutes, a porosity of about 9.2 sec./100 cc x 10^{-2} was obtained; whereas when the same pulp was refined for 40 minutes immediately after addition of the

enzyme (no standing), a porosity of about 12.4 sec. /100 cc x 10^{-2} was obtained. When the same pulp was allowed to stand for 24 hours and then washed clean of enzyme and refined for 40 minutes, a porosity of only 8.8 sec. /100 cc x 10^{-2} was obtained. In the absence of any enzyme before or after refining, 40 minutes of refining the same pulp produced a porosity of about 9.5 sec. /100 cc x 10^{-2}. The above examples clearly demonstrate the importance of beginning the refining action immediately after addition of the enzyme to the pulp. These examples also show the synergistic effect achieved by the simultaneous refining and enzymatic action of the present invention, as opposed to the process of subjecting the pulp to the refining and enzymatic action separately.

In other examples of the inventive process, various mixtures of an ammonia-base sulfite pulp, water, and cellase were refined in a Tappi beater. The temperature of the mixture was about 35°C, the pH was about 5.5, and the power input rate to the beater was about 1640 watts/hour. The proportions of pulp, water, and cellase employed in the various mixtures were as follows:

Run	Pulp	Water	Cellase
A	360 gm.	25,000 gm.	2.2 gm.
B	360 gm.	25,000 gm.	1.1 gm.
C	360 gm.	25,000 gm.	2.2 gm.
D	360 gm.	25,000 gm.	1.1 gm.

In runs A and B, all the cellase was added at the start of the beating period; in run C, 1.1 gm. was added to the start and 1.1 gm. after 20 minutes; and in run D, 0.35 gm. was added at the start and 0.25 gm. increments after 10, 20, and 30 minutes. The results of these runs, as determined by the standard Tappi procedure for beater evaluation, are presented graphically in Figs. 1, 2, and 3 along with the results of a "blank" run in which no enzyme was employed. Figs. 1 and 2 show the effect of the simultaneous refining and enzymatic action on the burst factor and breaking length of the pulp over a 40-minute beating period. The burst factor is an indication of the burst strength of the resultant paper formed from the refined pulp, and the breaking length is an indication of the

tensile strength of the resultant paper.

It can be seen from the curves in Figs. 1 and 2 that both the burst factor and the breaking length of the cellase-containing pulps increased at a faster rate than the blank pulp for at least the first 10 minutes, and after 20 minutes the cellase-containing pulps always had significantly higher burst factors and breaking lengths than the blank pulp. In many cases, the burst factor and breaking length levels achieved in the blank pulp after 40 minutes were achieved in the cellase-containing pulps after only 20-25 minutes. This indicates a possible saving of nearly 50% of the power required to beat the pulp to those values. It can be seen from the curves in Figs. 1 and 2 that the results were more favorable over the second 20 minutes of beating when the cellase was added in increments during the beating process, as in runs C and D.

Fig. 3 shows the effect of the cellase on porosity, as measured on paper hand-sheets made from the resultant pulp. Since porosity is expressed in units of time required for a given amount of air to pass through the sheet, a high value indicates a nonporous sheet. It can be seen from the curves in Fig. 3 that the cellase effected significant increases in the porosity value over practically the entire beating period. This obvious beneficial effect of the enzymatic action on porosity is of a large order of magnitude and is a result often desired in a large variety of papers. It provides the paper maker with the alternative of obtaining a much less porous sheet with the standard beating time or of getting the same porosity in about 1/3 to 1/2 the beating time required in the absence of enzymes.

In another example of the process, various mixtures of an ammonia-base sulfite pulp, water, and pectinol were refined in a Tappi beater. The temperature of the mixture was about 35°C, the pH was about 5.5, and the power input rate go the beater was about 1640 watts/hour. The proportions of pulp, water, and pectinol were as follows:

Run	Pulp	Water	Pectinol
E	360 gm.	25,000 gm.	2 ml.
F	360 gm.	25,000 gm.	2 ml.
G	360 gm.	25,000 gm.	2 ml.
H	360 gm.	25,000 gm.	2 ml.

All the pectinol was added at the start of the run in each case, but in run H the mixture was allowed to stand for 30 minutes before the beating action was started. The results of these runs are presented graphically in Figs. 4, 5, and 6 along with the results of a blank run in which no enzyme was employed. As can be seen from the curves in Figs. 4, 5, and 6, the effect of the pectinol on the burst factor, breaking length, and porosity in runs E, F, and G was similar to that of the cellase in runs C and D discussed above. However, run H, with no load on the beater arm for the first 30 minutes, shows that merely mixing the pectinol with the pulp and allowing the mixture to stand produces little or no improvement in the pulp properties. When the beater load was finally applied in run H, the rate of improvement in the pulp properties was practically the same as in the first 10 minutes of runs E, F, and G employing simultaneous refining and enzymatic action. This is definite evidence of the fact that improvement of strength and porosity development is the result of simultaneous refining and enzymatic action.

In further examples of the process, various batches of a mixture of an ammonia-base sulfite pulp, water, and Cellase (enzyme) were refined in a standard Tappi beater. The mixture contained about 360 gm. pulp, 25,000 gm. water, and 1 gm. enzyme. The enzyme was added to each batch at the start of the beating period. The temperature of the mixture was about 35°C and the pH was about 5.5. Instead of using the standard load on the beater arm, various percentages of load from zero to 75% were used with the different batches, and the power input to the beater was measured in all cases after various beating times. The recorded measurements are shown in the following table:

ACCUMULATED POWER (WATT-HR.) AT VARIOUS BEATER LOADS STANDARD SAMPLE TIMES

Power Input to Beater	-----		-----		-----		409 watts/hour		422 watts/hour		435 watts/hour	
Beater Load	0 Load		455 gm		910 gm		1360 gm		2720 gm		4080 gm	
% Standard Beater Load	0%		8.3%		16.5%		24.6%		49.2%		74.0%	
Beating Time	Blank	Enzyme	Blank	Enzyme	Blank	Enzyme	Blank	Enzyme	Blank	Enzyme	Blank	Enzyme
10	64.7	64.4	63.5	67.7	68.0	68.0	72.2	69.9	76.1	76.4	80.6	80.0
20	128.1	127.7	127.1	136.0	134.9	134.6	141.9	137.9	147.4	147.2	153.7	151.7
30	190.3	189.5	191.6	203.7	200.3	200.0	210.4	204.0	215.7	214.5	223.7	220.[illegible]
40	251.8	250.7	256.2	269.4	264.8	264.2	277.4	267.5	282.5	280.6	292.2	287.9

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In order to determine the effect of the power input rate and accumulated power on the pulp properties, hand sheets were prepared from samples taken periodically from each batch. These sheets were then tested for porosity and compared with similar sheets made from pulp which had been refined under the same conditions for the same periods without the use of an enzyme. The results of these tests are shown in Fig. 7 as a plot of the porosity difference between the blank and enzyme runs. As can be seen from the curves in Fig. 7, the degree of improvement achieved by the simultaneous refining and enzymatic action, compared with the refining action alone, increased rapidly with increasing power input rates and increasing accumulated power. Moreover, it can be seen that there was a minimum total power input rate to the equipment of about 400 watts per hour below which very little improvement was achieved by the use of the enzyme, regardless of the magnitude of the total accumulated power. At power input rates above this minimum level, the porosity difference between the blank and enzyme runs increased rapidly with increasing accumulated power levels.

While various specific embodiments of the present invention have been described herein in some detail, it will be understood that the same are susceptible of numerous modifications.

WHAT IS CLAIMED IS:

1. A process for treating paper pulp, which process comprises mixing said pulp with water and an enzyme and immediately refining the resulting mixture so as to subject said pulp to simultaneous refining and enzymatic action, whereby to improve the characteristics of paper produced from said pulp.

2. The process of claim 1 wherein said enzyme is selected from the group consiting of cellase, pectinol, lipase, pectinase, lysozyme, amylase, pectase, and hemi-cellulase.

3. The process of claim 1 wherein the concentration of enzyme in said mixture is at least about 10 parts per million by weight, based on the dry weight of said pulp.

4. The process of claim 1 wherein said mixture is refined at a temperature of between about 20°C and about 55°C.

5. The process of claim 1 wherein additional enzyme is added to said mixture periodically during said refining.

6. The process of claim 1 wherein the pH of said mixture is between about 3.5 and 5.5.

7. A process for improving the physical properties of wood pulp comprising suspending said pulp in water; adding an enzyme to the suspended pulp; and immediately mechanically working the resulting mixture of pulp, water, and enzyme so as to subject said pulp to simultaneous refining and enzymatic action.

8. A process for treating paper pulp to improve the properties of the paper produced therefrom, which process comprises mixing said pulp with

water and an enzyme, and immediately refining said pulp at a rate sufficient to disrupt the fiber structure of said pulp so as to provide intimate contact between said enzyme and the constituents of the fibers, thereby subjecting said pulp to simultaneous refining and enzymatic action.

9. A process for treating paper pulp which process comprises mixing said pulp with water and an enzyme, and immediately refining said pulp at a rate of at least about 45,000 watts per hour per ton of pulp, thereby subjecting said pulp to simultaneous refining and enzymatic action.

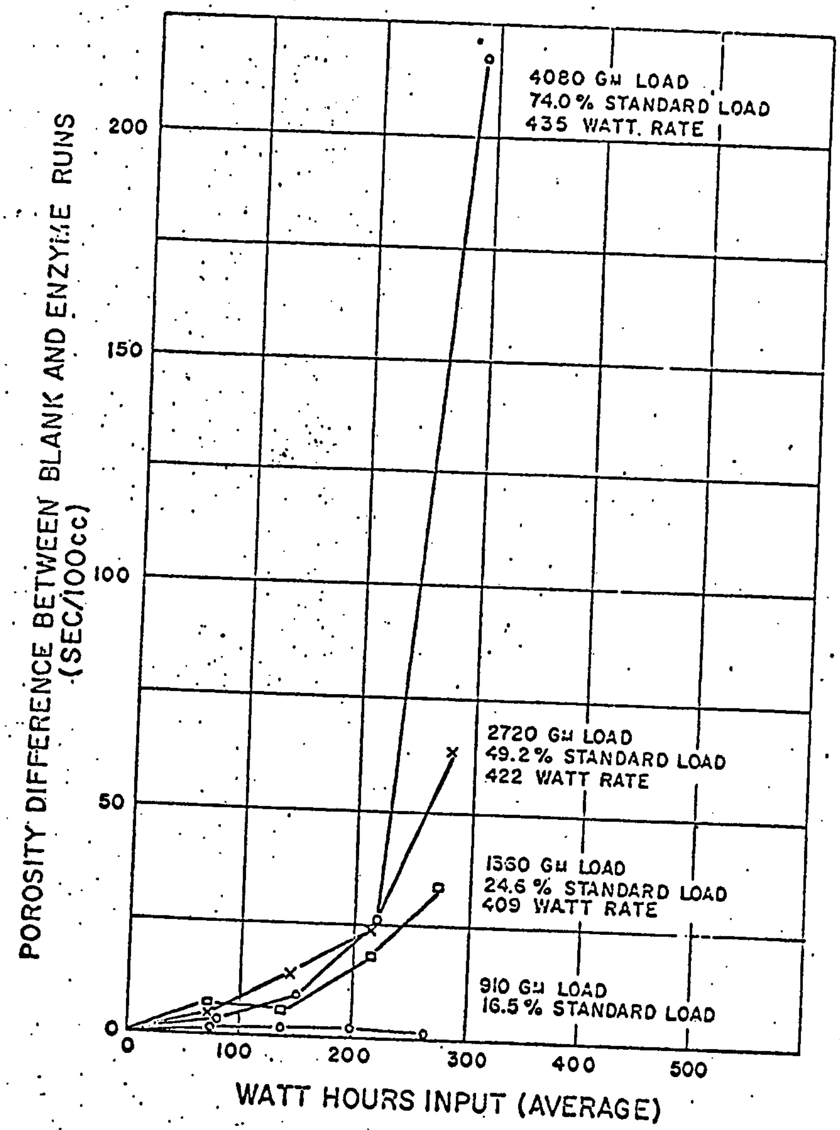
4080 GM LOAD
74.0 % STANDARD LOAD
435 WATT RATE
2720 GM LOAD
49.2 % STANDARD LOAD
422 WATT RATE
1360 GM LOAD
24.6 % STANDARD LOAD
409 WATT RATE
910 GM LOAD
16.5 % STANDARD LOAD
POROSITY DIFFERENCE BETWEEN BLANK AND ENZYME RUNS (SEC/100cc)
0
50
100
150
200
0
100
200
300
400
500
WATT HOURS INPUT (AVERAGE)

Fig. 7.

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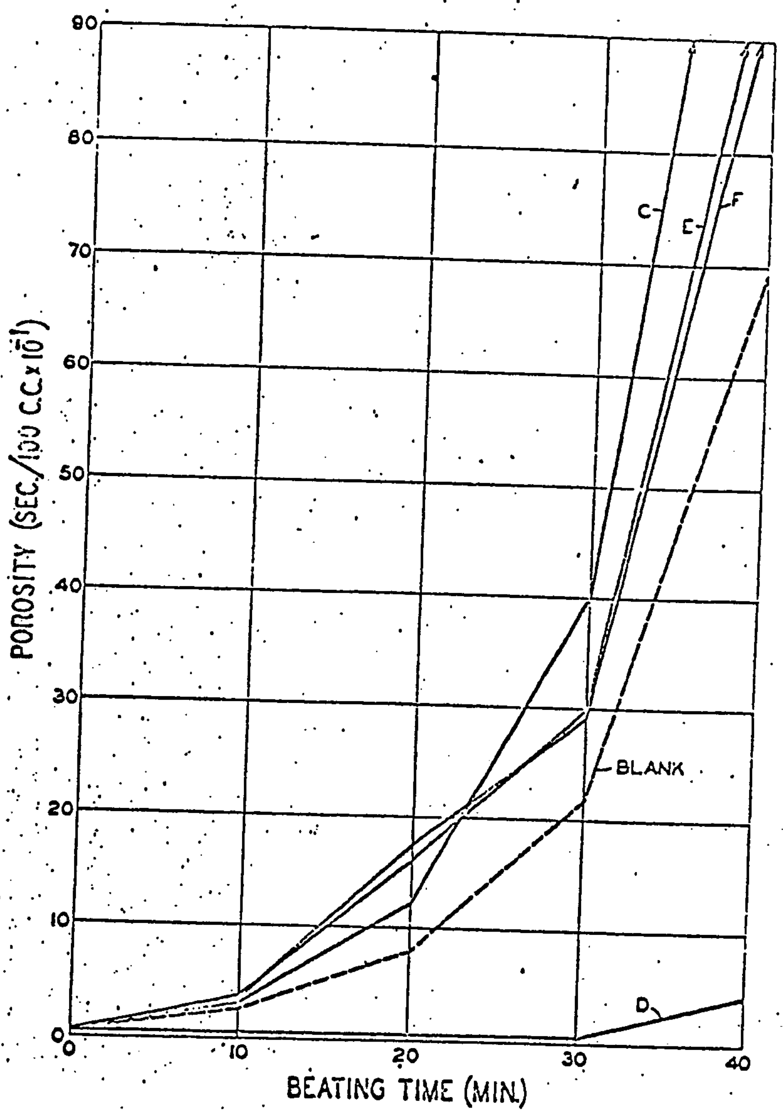

Fig. 6.

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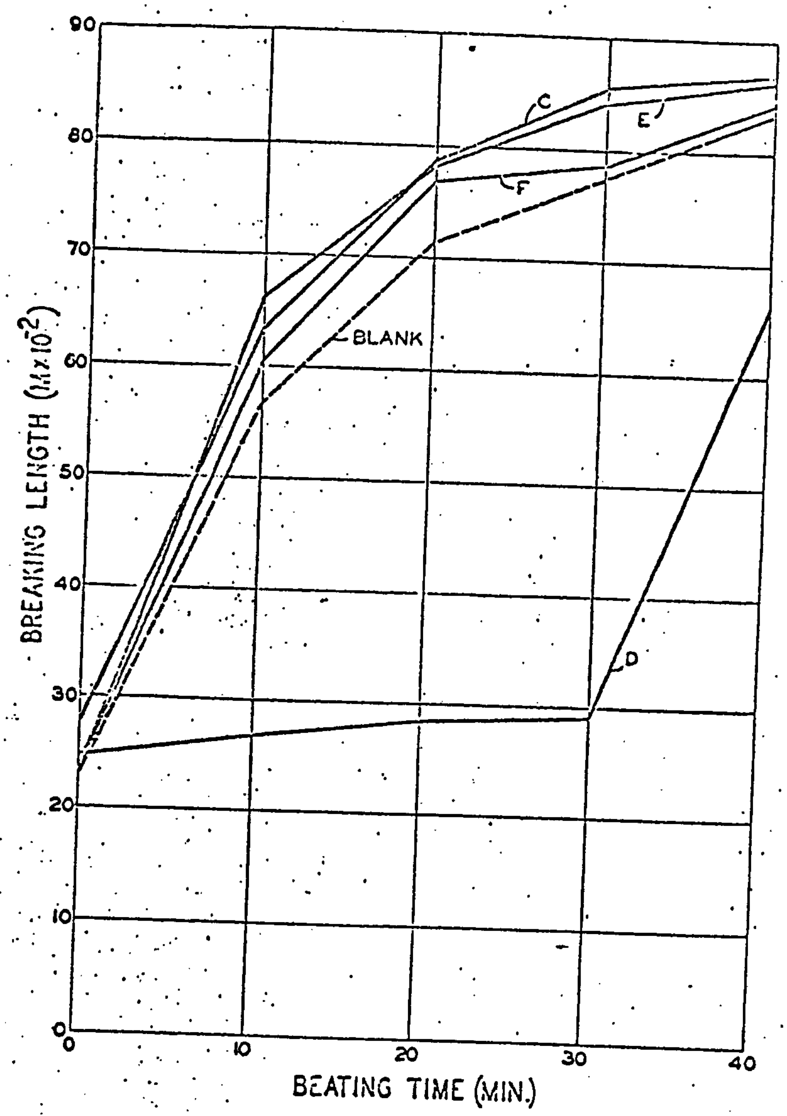

Fig. 5.

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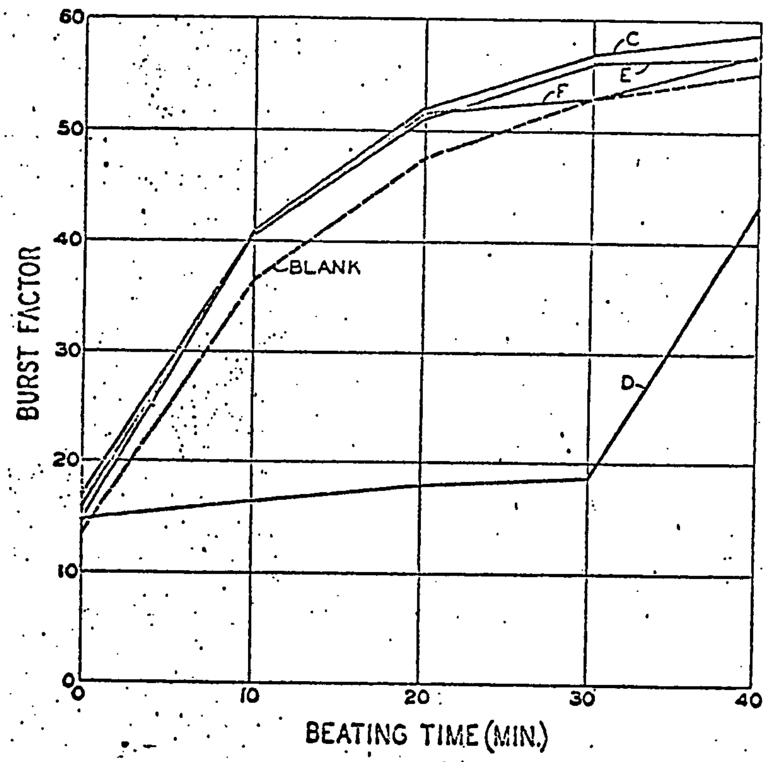

Fig. 4.

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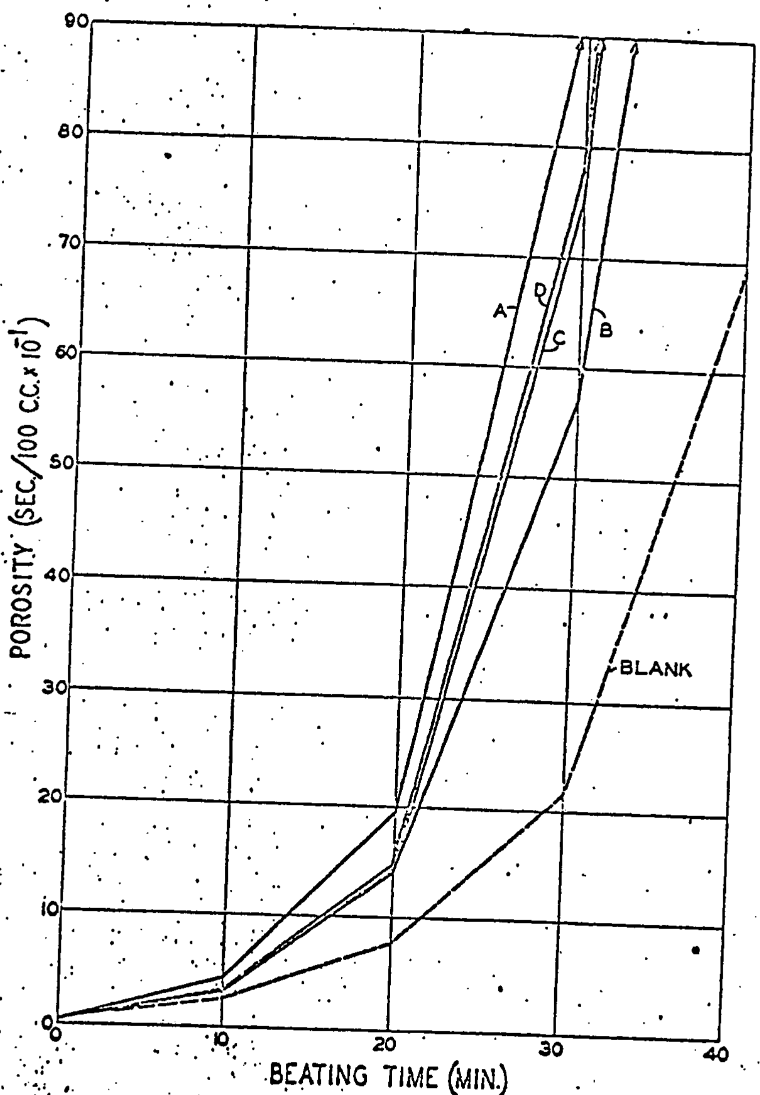

Fig. 3.

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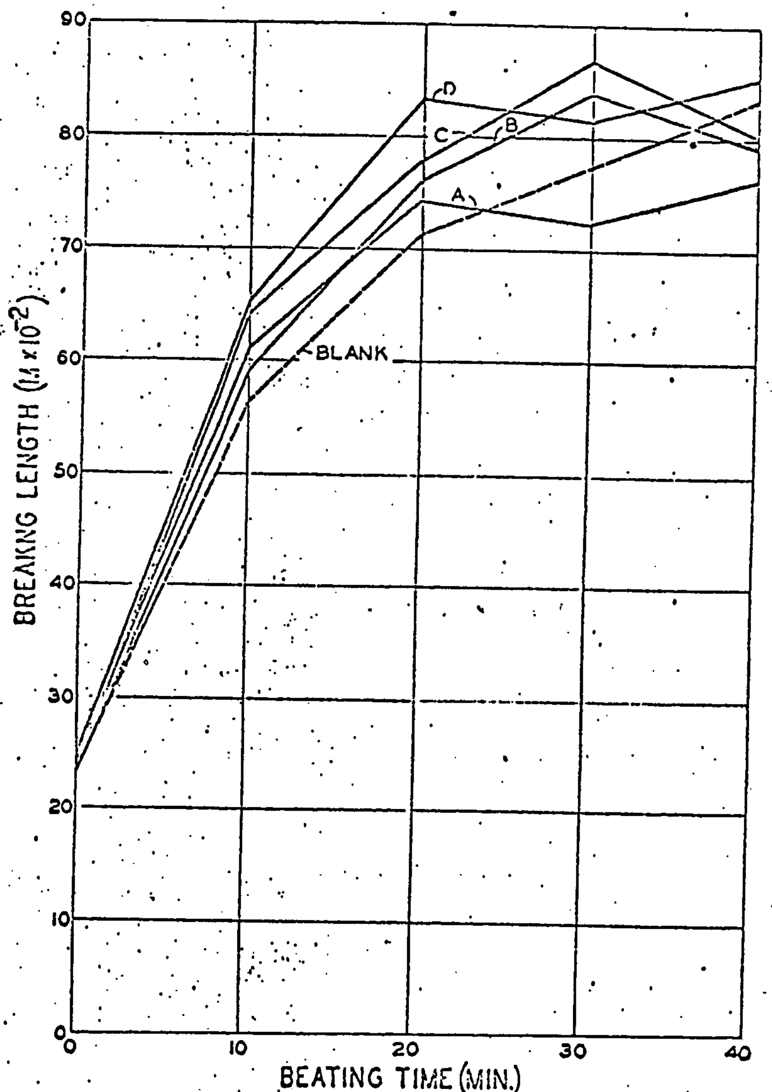

Fig. 2.

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PROCESS FOR TREATING PAPER PULP

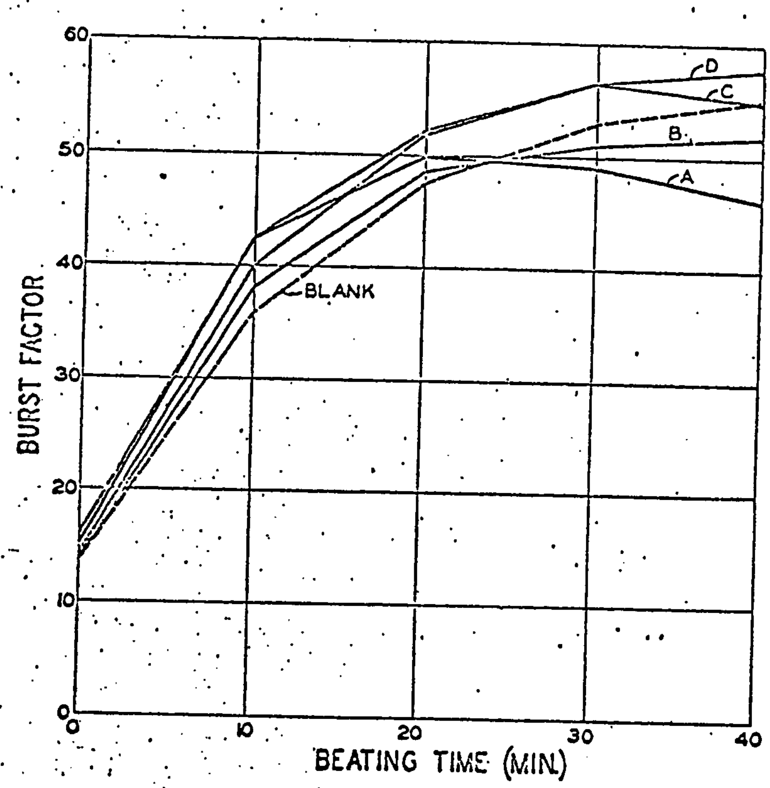

Fig. 1.